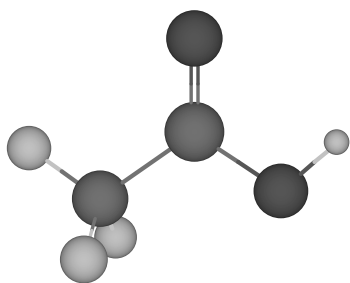
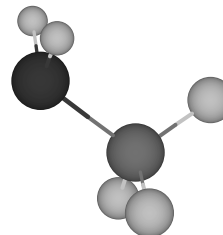


Acids and Bases



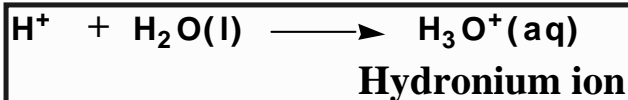
Chapter 4



1

Arrhenius Acids and Bases

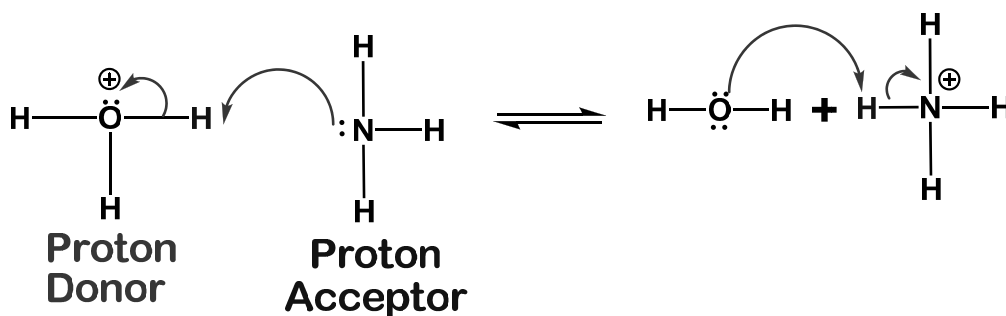
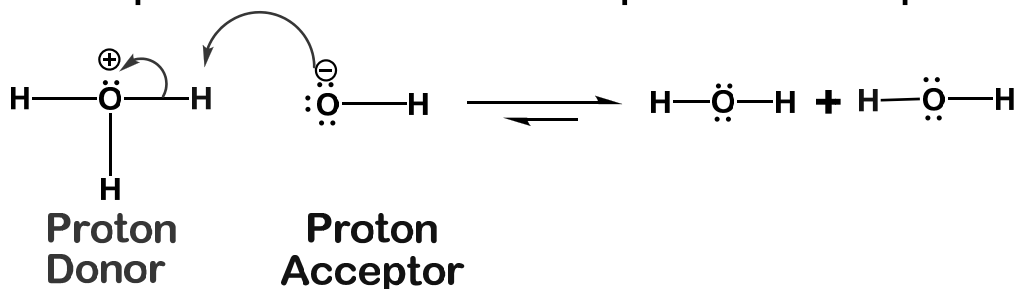
- In 1884, Svante Arrhenius proposed these definitions
 - **acid:** A substance that produces H_3O^+ ions aqueous solution.
 - **base:** A substance that produces OH^- ions in aqueous solution.
 - this definition of an acid is a slight modification of the original Arrhenius definition, which was that an acid is a substance that produces H^+ in aqueous solution.
 - today we know that H^+ reacts immediately with a water molecule to give a **hydronium ion**.



2

Brønsted-Lowry Definitions

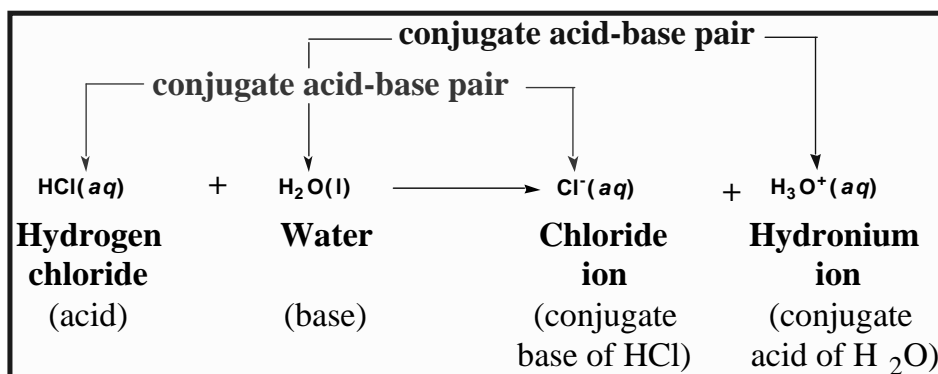
Acid: proton donor. Base: proton acceptor.



3

Conjugate Acids & Bases

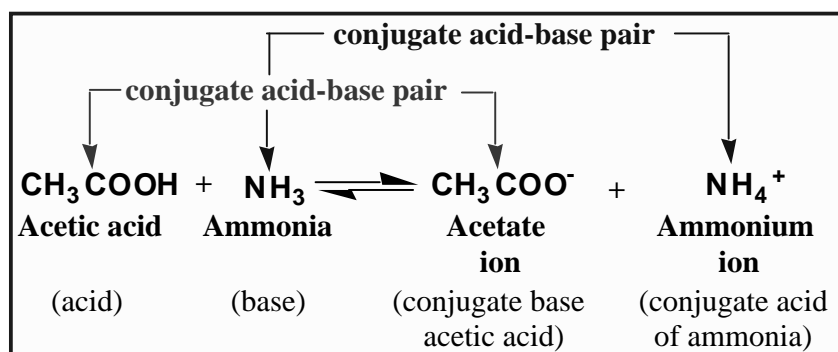
- **Conjugate base:** The species formed from an acid when it donates a proton to a base.
- **Conjugate acid:** The species formed from a base when it accepts a proton from an acid.
- **Acid-base reaction:** A proton-transfer reaction.
- **Conjugate acid-base pair:** Any pair of molecules or ions that can be interconverted by transfer of a proton.



4

Conjugate Acids & Bases

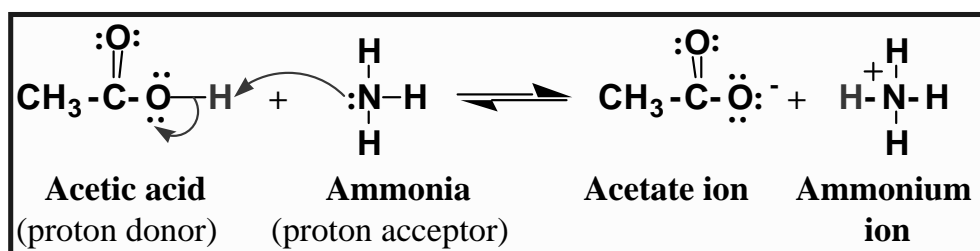
- Brønsted-Lowry definitions do not require water as a reactant.
- Consider the following reaction between acetic acid and ammonia.



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Acids & Bases

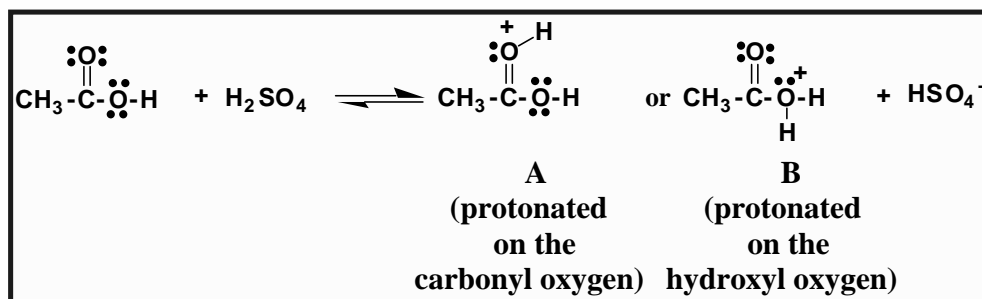
- Use curved arrows to show the flow of electrons in an acid-base reaction.



6

Resonance in Acids

- Many organic molecules have two or more sites that can act as proton acceptors.
 - In this chapter, discussion is limited to carboxylic acids, esters, and amides.
 - In these molecules, **the favored site of protonation is the one in which the charge is more delocalized.**
 - Question: Which oxygen of a carboxylic acid is protonated?

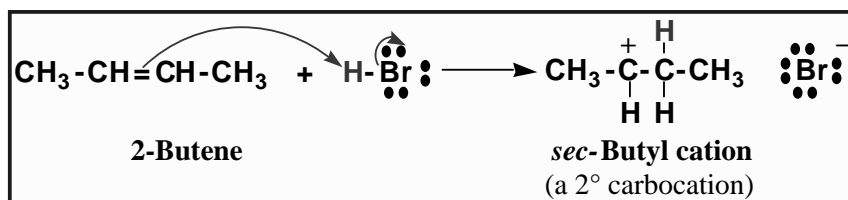


7

π Electrons As Basic Sites

Proton-transfer reactions occur with compounds having π electrons, as for example the π electrons of carbon-carbon double and triple bonds.

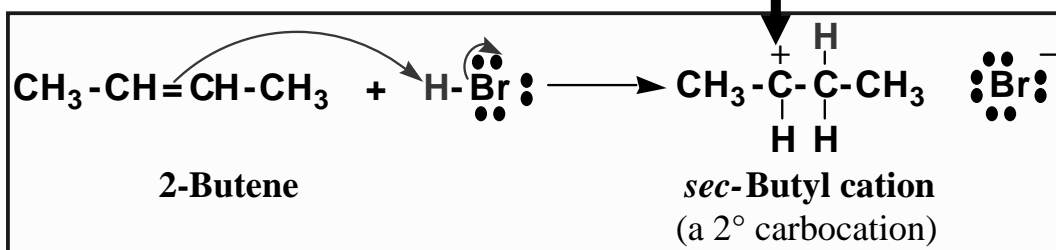
The pi electrons of 2-butene, for example, react with HBr by proton transfer to form a new C-H bond.



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π Electrons As Basic Sites

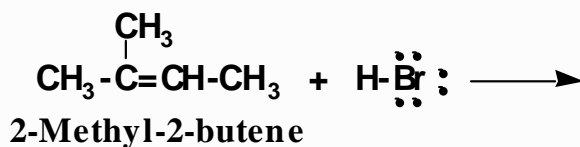
The result is formation of a carbocation, a species in which one of its carbons has only six electrons in its valence shell and carries a charge of +1.



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π Electrons As Basic Sites

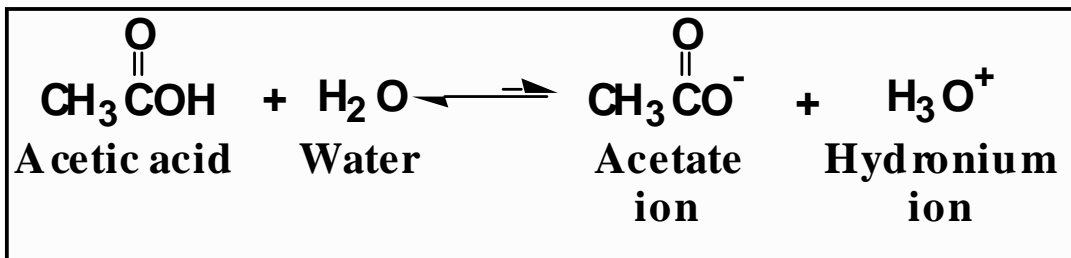
Sample Problem: Draw Lewis structures for the two possible carbocations formed by proton transfer from HBr to 2-methyl-2-butene.



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Acids & Base Strengths

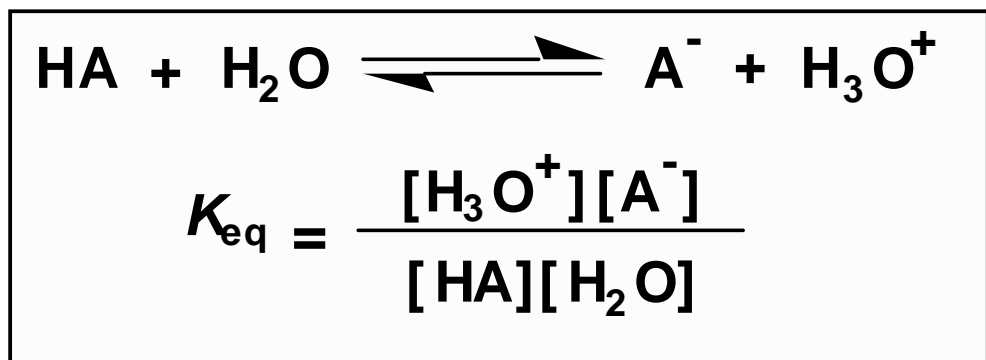
- The strength of an acid is expressed by an equilibrium constant.
 - the acid dissociation of acetic acid is given by the following equation.



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Weak Acids and Bases

An equilibrium expression for the dissociation of any uncharged acid, HA, is written as:





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Weak Acids and Bases

- Water is a solvent and its concentration is a constant equal to approximately 55.5 mol/L.
- We can combine these constants to give a new constant, K_a , called an acid dissociation constant.

$$K_a = K_{eq}[\text{H}_2\text{O}] = \frac{[\text{H}_3\text{O}^+][\text{A}^-]}{[\text{HA}]}$$

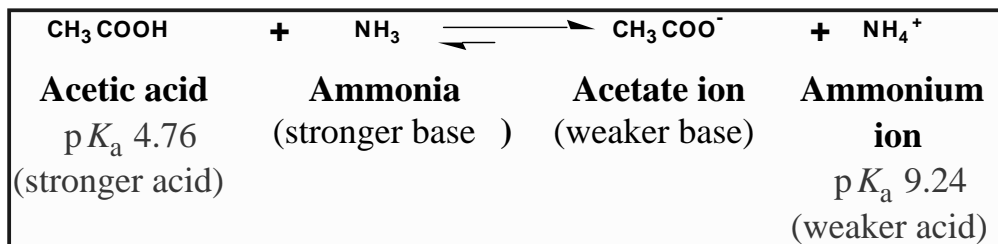
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pK_a					
Weaker acid	Acid	Formula	pK _a	Conjugate Base	Stronger conjugate base
	Ethane	CH ₃ CH ₃	51	CH ₃ CH ₂ ⁻	
	Ethylene	CH ₂ =CH ₂	44	CH ₂ =CH ⁻	
	Ammonia	NH ₃	38	NH ₂ ⁻	
	Hydrogen	H ₂	35	H ⁻	
	Acetylene	HC≡CH	25	HC≡C ⁻	
	Ethanol	CH ₃ CH ₂ OH	15.9	CH ₃ CH ₂ O ⁻	
	Water	H ₂ O	15.7	HO ⁻	
	Methylammonium ion	CH ₃ NH ₃ ⁺	10.64	CH ₃ NH ₂	
	Bicarbonate ion	HCO ₃ ⁻	10.33	CO ₃ ²⁻	
	Phenol	C ₆ H ₅ OH	9.95	C ₆ H ₅ O ⁻	
	Ammonium ion	NH ₄ ⁺	9.24	NH ₃	
	Hydrogen sulfide	H ₂ S	7.04	HS ⁻	
	Carbonic acid	H ₂ CO ₃	6.36	HCO ₃ ⁻	
	Acetic acid	CH ₃ COOH	4.76	CH ₃ COO ⁻	
	Benzoic acid	C ₆ H ₅ COOH	4.19	C ₆ H ₅ COO ⁻	
	Phosphoric acid	H ₃ PO ₄	2.1	H ₂ PO ₄ ⁻	
	Hydronium ion	H ₃ O ⁺	-1.74	H ₂ O	
	Sulfuric acid	H ₂ SO ₄	-5.2	HSO ₄ ⁻	
	Hydrogen chloride	HCl	-7	Cl ⁻	
	Hydrogen bromide	HBr	-8	Br ⁻	
	Hydrogen iodide	HI	-9	I ⁻	
Stronger acid					Weaker conjugate base


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Acid-Base Equilibria

- Equilibrium favors reaction of the stronger acid and stronger base **to give** the weaker acid and weaker base.



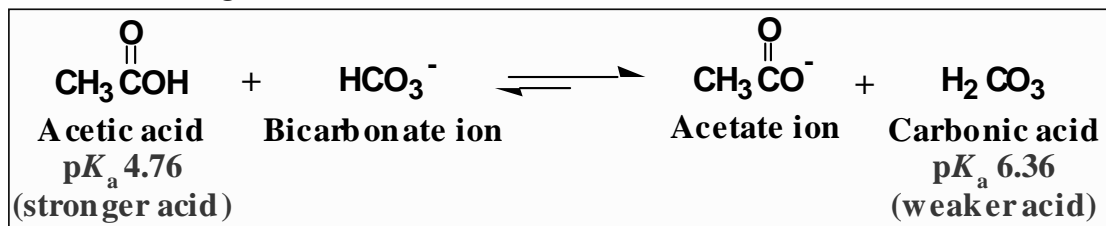
Favors the side with the highest pKa
(i.e weaker acid)



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Acid-Base Equilibria

- Consider the reaction between acetic acid and sodium bicarbonate.
 - write the equilibrium as a net ionic equation.
 - omit Na^+ because it does not undergo any chemical change in the reaction.



- Equilibrium lies to the right.
- Carbonic acid forms, which then decomposes to carbon dioxide and water.

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Thermochemistry & Mechanisms

- **Reaction mechanism:** A step-by-step description of how a chemical reaction occurs.
- **Thermochemistry:** The study of the energy of an entire system at each and every instant of a reaction.
- **Reaction coordinate diagram:** A graph showing the energy changes that occur during a chemical reaction. Energy is plotted on the vertical axis and reaction progress (time) is plotted along the horizontal axis.

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Thermochemistry & Mechanisms

- **Most chemical reactions occur via collisions.**
 - During collisions, the structure of a molecule contorts and flexes. Collisions of higher energy lead to larger distortions in structure.
 - During collisions, the kinetic energy of the reactants is converted to potential energy, which is stored in the chemical structures in the form of structural strains.

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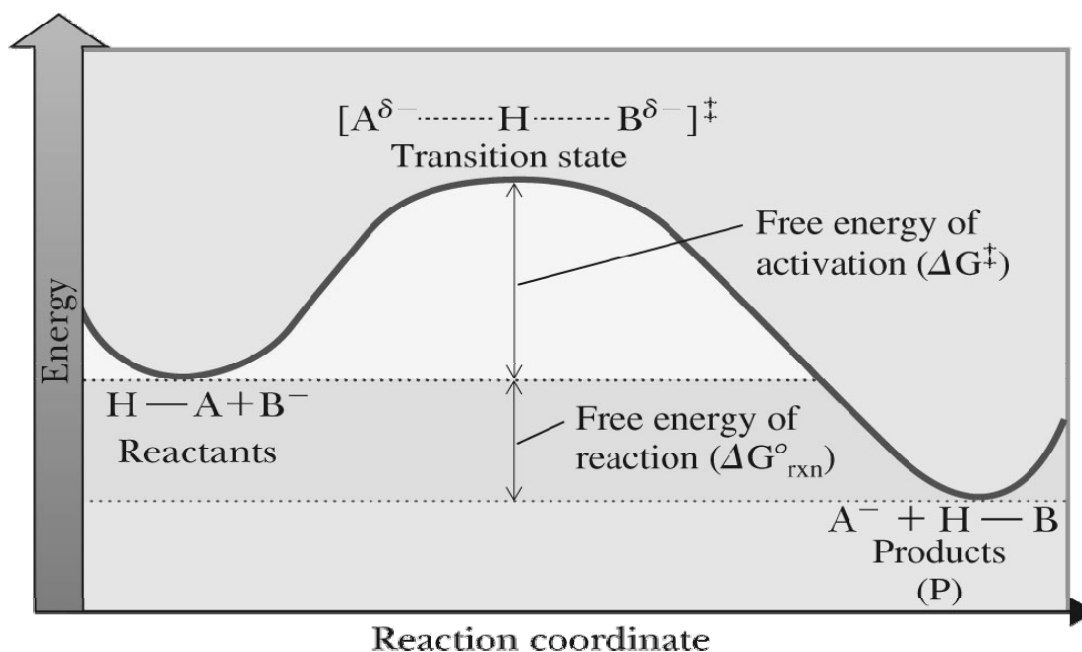
Thermochemistry & Mechanisms

- During a collision process that yields a reaction, a transition state (\neq) is formed which possesses partially broken and partially formed bonds.
- Chemists use reaction coordinate diagrams to show the changes in energy for the molecules involved in a chemical reaction.

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Thermochemistry & Mechanisms

A reaction coordinate diagram for a one step reaction between H-A and B.



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Thermochemistry & Mechanisms

- For reactions at constant pressure, the change in Gibbs free energy, ΔG° , is used.
 - This kind of energy controls the rates and equilibrium of reactions.
 - The change in Gibbs free energy between reactants and products is related to the equilibrium constant through this equation:

$$\Delta G^\circ = -RT \ln K_{eq}$$

where $R = 8.31 \text{ J/K mol}$ and T is the temperature in kelvins.

- **Free energy of activation:** The difference in energy between reactants and the transition state.

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Molecular Structure and Acidity

- The overriding principle in determining the relative acidities of uncharged organic acids is the stability of the anion, A^- , resulting from the loss of a proton.
 - **the more stable the anion, the greater the acidity of HA**

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Molecular Structure and Acidity

- Ways to stabilize anions include having the negative charge:
 - on a more electronegative atom.
 - on a larger atom.
 - delocalized through resonance.
 - delocalized by the inductive effect.
 - in an orbital with more s character.

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Electronegativity

1. Electronegativity of the atom bearing the negative charge

Within a period, the greater the electronegativity of the atom bearing the negative charge, the more strongly its electrons are held, the more stable the anion is, and the stronger the acid.

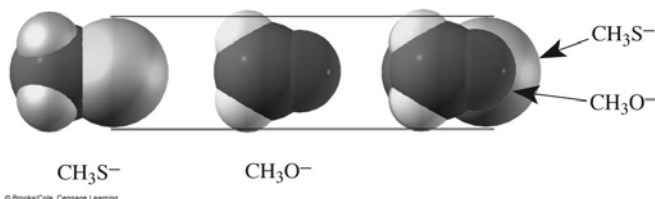
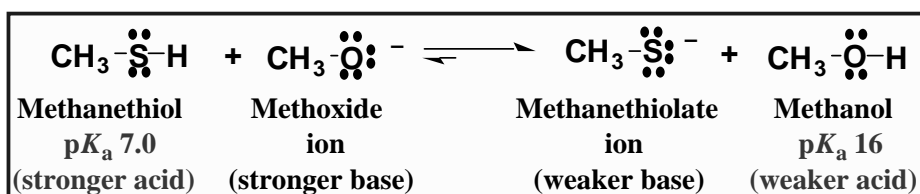
Acid		Conjugate base
Methanol pK_a 16	$\text{CH}_3-\ddot{\text{O}}-\text{H}$	$\text{CH}_3-\ddot{\text{O}}:^-$ Methoxide ion
Methylamine pK_a 38	$\text{CH}_3-\ddot{\text{N}}-\text{H}$ H	$\text{CH}_3-\ddot{\text{N}}:^-$ Methylamide ion H
Ethane pK_a 51	$\text{CH}_3-\text{C}-\text{H}$ H	$\text{CH}_3-\text{C}:^-$ Ethyl anion H

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Size of the atom

2. Size of the atom bearing the negative charge

- The larger the atom bearing the charge, the greater its stability.

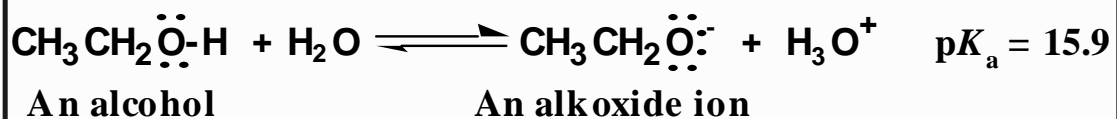


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Resonance delocalization

3. Resonance delocalization of charge in A^-

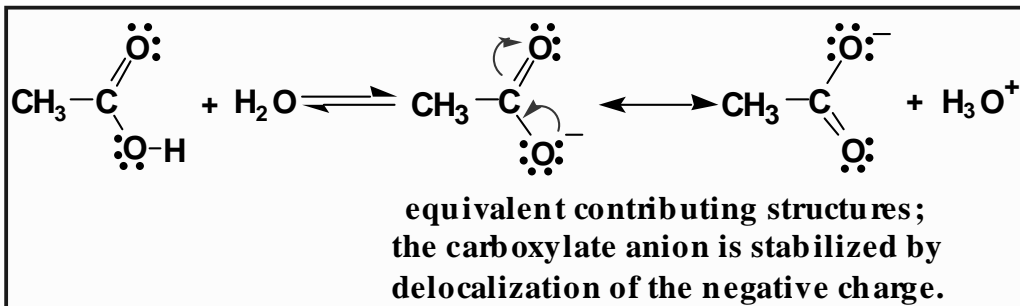
- The more stable the anion, the farther the position of equilibrium is shifted to the right.
- Compare the acidity alcohols and carboxylic acids.
- Ionization of the O-H bond of an alcohol gives an anion for which there is no resonance stabilization:



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Resonance delocalization

- Ionization of a carboxylic acid gives a resonance-stabilized anion.
- The pK_a of acetic acid is 4.76



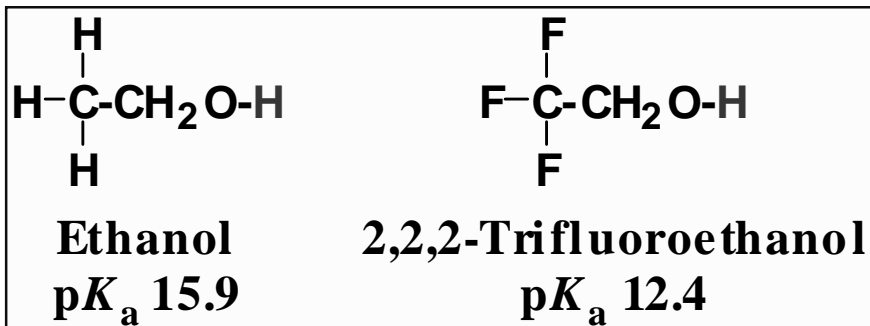
- Carboxylic acids are stronger acids than alcohols as a result of the resonance stabilization of the carboxylate anion.

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e^- withdrawing inductive effect

4. Electron-withdrawing inductive effect

- The polarization of electron density of a covalent bond due to the electronegativity of an adjacent covalent bond.



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e⁻ withdrawing inductive effect

4. Electron-withdrawing inductive effect

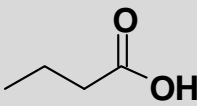
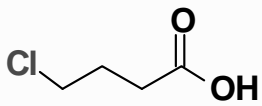
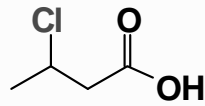
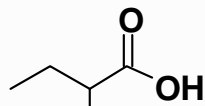
- Stabilization by the inductive effect falls off rapidly with increasing distance of the electronegative atom from the site of negative charge in the conjugate base.

CF₃-CH₂-OH	CF₃-CH₂-CH₂-OH	CF₃-CH₂-CH₂-CH₂-OH
2,2,2-Trifluoro-ethanol	3,3,3-Trifluoro-1-propanol	4,4,4-Trifluoro-1-butanol
(pK_a 12.4)	(pK_a 14.6)	(pK_a 15.4)

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e⁻ withdrawing inductive effect

- the operation of the inductive effect in the acidity of halogen substituted **carboxylic acids** is also observed:

			
Butanoic acid pK_a 4.82	4-Chlorobutanoic acid pK_a 4.52	3-Chlorobutanoic acid pK_a 3.98	2-Chlorobutanoic acid pK_a 2.83

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Hybridization (of the anion)

5. Hybridization

- For anions differing only in the hybridization of the charged atom, the **greater the percentage s character to the hybrid orbital of the charged atom, the more stable the anion.**

Weak Acid		Conjugate Base	pK_a	Increasing acidity
Water	HO-H	HO ⁻	15.7	
Alkyne	HC≡C-H	HC≡C ⁻	25	
Ammonia	H ₂ N-H	H ₂ N ⁻	38	
Alkene	CH ₂ =CH-H	CH ₂ =CH ⁻	44	
Alkane	CH ₃ CH ₂ -H	CH ₃ CH ₂ ⁻	51	

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In summary:

1. Negative charge on the more electronegative atom.
2. Negative charge on a larger atom.
3. Delocalization of the negative charge through resonance.
4. Delocalization of the negative charge onto electron-withdrawing groups by the inductive effect.
5. Have the negative charge in an orbital with more s character.

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